

Cohesive and Thermal Properties of Sodium Cyanide-Halide Mixed Crystals

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ABSTRACT

In order to analyse the cohesive and thermal properties of sodium cyanide-halide mixed crystals an Extended Three Body Force Shell Model (ETSM) has been applied by incorporating the effect of translational-rotational (TR) coupling. We have conducted theoretical research on cohesive and thermal properties, such as cohesive energy (ϕ), molecular force constant (f), compressibility (β), Reststrahlen frequency (ν_0), Debye temperature (θ_D), Gruneisen parameter (γ), Moelwyn Hughes constants (F_1) and the ratio of volume thermal expansion coefficient (α_v) to volume specific heat (C_v), as a function of temperature within the temperature range $50\text{K} \leq T \leq 300\text{K}$ at concentration $x=0, 0.27, 0.58$ and 1 . The current model computations and the findings of the available experiments are in good agreement. The ETSM is a sufficiently realistic model and may be applied to a variety of other mixed crystals in this family.

Keywords: Cohesive; Thermal; Debye temperature; ODM's; Sodium Cyanide; Sodium halide.

1. Introduction

The Sodium cyanide-halide mixed crystals are convenient material for studying disordered phenomena. At room temperature, the NaCN compound exhibits a rock salt structure shown in figure 1, where dumbbell-shaped (CN^-) ions are orientationally disordered [1]. The systems retain their crystalline order, making them simpler to model than amorphous solids and their degree of disorder can be easily changed by varying the concentration of constituents. These mixed systems show glassy behavior at low temperatures and over a wide range of concentrations [2]. The present theoretical work has been carried out on the system $(\text{NaBr})_{1-x}(\text{NaCN})_x$. At room temperature, these crystals have an orientationally disordered cubic structure.

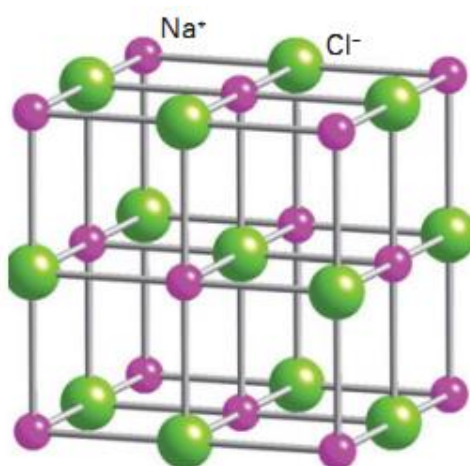


Figure 1. The rock-salt structure is a simple crystal structure of the form AX, it is adopted by sodium chloride [<http://openchemistryhelp.blogspot.com/2012/08/rock salt structure.html>]

We have applied the Extended Three Body Force Shell Model (ETSM) [3] by incorporating the effect of translational-rotational (TR) coupling for the study of cohesive and thermal properties of sodium cyanide-halide mixed crystals. It has been successful in describing the cohesive, thermal and dynamic properties of many

Orientationally Disordered alkali cyanides, alkali superoxide, C_{60} materials [3-10]. The interaction potential used to derive ETSM is given in the next section. The results and discussion are given in the subsequent section.

2. Theory of ETSM

The interaction potential used to derive the framework of the present ETSM can be expressed as [29],

$$\phi = -\frac{e^2}{2} \sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} \left[1 + \sum_{kk'} f_k(r_{kk'}) \right] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} - b \sum_{kk'} \beta_{kk'} \exp \left\{ \frac{r_k + r_{k'} - r_{kk'}}{\rho} \right\} + \phi^{TR} \quad (1)$$

Here k, k' denote the positive and negative ions respectively and the sum is taken over all the ions. In the above expression, the first two terms represent the long-range coulomb and three-body interaction (TBI) [20]. The third and fourth terms are vdW coefficients due to dipole-dipole and dipole-quadrupole (d-q) interactions with $c_{kk'}$ and $d_{kk'}$ as the corresponding vdw coefficient respectively.

The fifth term is Hafemeister and Flygare (HF) type [20] short-range (SR) overlap repulsion extended operative upto the second neighbour (nn) ion with $\beta_{kk'}$ as Pauling coefficient. Φ^{TR} is the contribution due to translational-rotational (TR) coupling effects [21, 22]. The range and hardness (b and ρ) parameters determined from the equilibrium condition,

$$[d\phi(r)/dr]_{r=r_0} = 0 \quad (2)$$

where r is the nearest interionic separation and r_0 is the equilibrium separation and the bulk modulus,

$$B = (9Kr_0)^{-1} [d^2\phi(r)/dr^2]_{r=r_0} \quad (3)$$

with K as the crystal structure constant ($K=2$ for NaCl structure).

The other parameters already discussed in the beginning are computed on the lines of Singh and Gaur [3].

3. Results and Discussion

Using the values of input data for pure NaCN and NaBr [23-30] listed in Table-I, values at different compositions and temperatures have been calculated by applying the well-known Vegard's law [31] and thermodynamics.

Table I. Input data for pure NaCN and NaBr.

Properties	NaCN	NaBr
r_0 (Å)	2.946	2.989
c_{11} (10^{11} dyne/cm ²)	2.534	4.800
c_{12} (10^{11} dyne/cm ²)	1.440	0.986
c_{44} (10^{11} dyne/cm ²)	0.03	1.070
C (10^{-60} erg cm ⁶)	251.19	429.3
D (10^{-76} erg cm ⁸)	89.52	207.0

We have computed the model parameters b , ρ and $f(r)$ using the Eq. (2-3) and second-order elastic constants, listed them in Table-II and using model parameters we have calculated the cohesive energy (ϕ), molecular force constant (f), compressibility (β), Reststrahlen frequency (ν_0), Debye temperature (θ_D), Gruneisen parameter (γ), Moelwyn Hughes constants (F_1), and the ratio of volume expansion coefficient (α_v) to volume specific heat (C_v) at temperature $50K \leq T \leq 300K$ for the composition $x=0, 0.27, 0.58$ and reported in Table (III-VI).

Table II. Model parameters for $(NaBr)_{1-x}(NaCN)_x$ at room temperature

Parameter	$x = 0$	$x = 0.27$	$x = 0.58$	$x = 1.0$
b (10^{-12} erg)	0.261	0.340	0.427	0.537
ρ (\oplus)	0.344	0.345	0.346	0.348
f (r)	0.0144	-0.541	-0.131	-0.0231

Table III. Cohesive and thermal properties of $(NaBr)_{1-x}(NaCN)_x$ at $x = 0$ ($50K \leq T \leq 300K$)

T(K)	ϕ (kJ/ mol ⁻¹)	f (10^4 dyn .cm ⁻¹)	β (10^{-12} dyn.cm ⁻¹)	ν_0 (THz)	θ_D (K)	α_v/c_v (10^3 J)	γ	F_1
50	-731.70	1.884	9.519	4.195	201.40	5.110	1.903	8.879
100	-728.90	1.837	9.850	4.143	198.90	5.123	1.932	9.238
150	-726.40	1.796	10.130	4.096	196.60	5.067	1.965	9.635
200	-723.70	1.757	10.420	4.052	194.50	5.020	1.997	10.03
250	-721.00	1.720	10.710	4.008	192.40	4.992	2.026	10.40
300	-718.31	1.686	10.990	3.969	190.50	4.798	2.058	10.80
300expt	-732.00 ¹⁹						1.64 ²³	

Table IV. Cohesive and thermal properties of $(NaBr)_{1-x}(NaCN)_x$ at $x = 0.27$ ($50K \leq T \leq 300K$)

T(K)	ϕ (kJ/ mol ⁻¹)	f (10^4 dyn .cm ⁻¹)	β (10^{-12} dyn.cm ⁻¹)	ν_0 (THz)	θ_D (K)	α_v/c_v (10^3 J)	γ	F_1
50	-732.70	1.874	9.540	4.200	201.85	5.298	1.903	8.879
100	-729.90	1.874	9.850	4.154	199.00	5.185	1.932	9.238
150	-727.12	1.873	10.130	4.101	196.88	5.148	1.965	9.635
200	-724.00	1.873	10.425	4.092	195.06	5.102	1.997	10.03
250	-722.51	1.873	10.717	4.064	192.95	5.054	2.026	10.40
300	-719.19	1.872	10.905	3.992	191.20	4.989	2.058	10.80

Table V. Cohesive and thermal properties of $(\text{NaBr})_{1-x}(\text{NaCN})_x$ at $x = 0.58$ ($50\text{K} \leq T \leq 300\text{K}$)

T(K)	ϕ (kJ/mol ⁻¹)	f (10 ⁴ dyn.cm ⁻¹)	β (10 ⁻¹² dyn.cm ⁻¹)	ν_0 (THz)	Θ_D (K)	α_v/c_v (10 ³ J)	γ	F_1
50	-733.79	1.884	9.565	4.195	206.32	5.331	1.903	8.879
100	-731.52	1.837	9.889	4.130	199.24	5.225	1.932	9.238
150	-727.98	1.790	10.140	4.096	196.60	5.191	1.965	9.635
200	-726.38	1.750	10.429	4.055	195.50	5.149	1.997	10.03
250	-723.00	1.722	10.821	4.000	193.40	5.102	2.026	10.40
300	-721.11 721.11	1.68	10.994	3.969	192.00	5.083	2.058	10.80

Table VI. Cohesive and thermal properties of $(\text{NaBr})_{1-x}(\text{NaCN})_x$ at $x = 1.0$ ($50\text{K} \leq T \leq 300\text{K}$)

T(K)	ϕ (kJ/mol ⁻¹)	f (10 ⁴ dyn.cm ⁻¹)	β (10 ⁻¹² dyn.cm ⁻¹)	ν_0 (THz)	Θ_D (K)	α_v/c_v (10 ³ J)	γ	F_1
50	-737.05	1.884	9.628	4.195	207.00	5.431	1.903	8.879
100	-735.20	1.837	9.902	4.130	200.00	5.423	1.932	9.238
150	-729.80	1.790	10.231	4.096	198.08	5.409	1.965	9.635
200	-728.56	1.750	10.495	4.055	196.89	5.398	1.997	10.03
250	-727.00	1.722	10.883	4.000	195.00	5.391	2.026	10.40
300	-722.80	1.68	11.006	3.969	193.58	5.382	2.058	10.80
300exptt	-738 ²⁸						2.46 ³³	

Our ETSM results show that cohesive energy decreases with increase in temperature. Negative values of cohesive energy show the stability of the compound. It is also observed that the Reststrahlen frequency and Debye temperature decrease with the increase in temperature. Lower values of Debye temperature give lower frequencies.

The Gruneisen parameter increase with an increase in temperature. The values of the Gruneisen parameter are below 2 as suggested in the literature. The compressibility (β), ratio of volume expansion coefficient (α_v) to volume specific heat (C_v), molecular force constant and Moelwyn Hughes constant which are directly derived from the cohesive energy show an increasing trend with temperature.

This trend is due to the increase in interionic separation. The results of cohesive energy and the Gruneisen parameter at $x=1.0$ are in good agreement with the experimental data available only at room temperature. Finally, the ETSM seems to be more realistic model for explaining cohesive and thermal properties of Orientationally Disordered Materials (ODMs).

Declarations

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Competing Interests Statement

The author declares no competing financial, professional, or personal interests.

Consent for publication

The author declares that he/she consented to the publication of this research work.

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